CHAPTER III
REMOVAL OF HALOACETIC ACIDS BY OZONE-BIOLOGICAL
ACTIVATED CARBON (BAC)

3.1. Introduction

Haloacetic acids are disinfection by products (DBPs) formed after the addition of chlorine compounds such as hypochlorous acid, hypochlorite, or dichlorine to water or wastewater for disinfection purpose (Urbanski, 2001). Reactions between natural organic matter (NOM) and chlorine compounds produced haloacetic acids at ppt to ppb level in drinking water distribution system and in ppb to ppm range in wastewater (McRae et al., 2000; Rebhun, et al., 1989). Haloacetic acids receive a considerable attention due to their potential as a probable human carcinogen (USEPA 1999). Trichloroacetic acid (TCAA) and monochloroacetic acid (CAA) are phytotoxic and were used as herbicides until the late 1980s (Berg et al., 2000). Haloacetic acids also found toxic to aquatic organisms (Hanson et al., 2000, 2002). The concern over their carcinogenicity led the United State Environment Protection Agency (USEPA) to begin regulate the allowable concentration of haloacetic acids in drinking water as part of its Disinfectants and Disinfection byproducts (D/DBP) Rule promulgated in 1998 (USEPA, 1998). Five haloacetic acids, known as HAA$_5$, are regulated as part of the rule: monochloroacetic acid (CAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromoacetic acid (BAA), and dibromoacetic acid (DBAA). HAA$_5$, which is expressed as the sum of the concentrations of these acids is currently limited to 60 ppb. It is anticipated the USEPA will soon lower the concentration limit to 30 ppb in the Stage 2 of the D/DBP Rule (Xie, 2004).

Haloacetic acids in water supply are commonly controlled through enhanced coagulation/softening processes that remove their precursor (*i.e.*, NOM) before disinfection process. However, haloacetic acids in processed water still remain in a detectable level. The concentration of HAA$_5$ in Bangkok water supply, sampling at the chlorination station, Bangkhen water treatment plant is approximately 50 ppb. It has been reported that approximately 16 % of water treatment plants affiliated with the American Water System (AWS) would soon have HAA$_5$ exceed 60 ppb and will face a major problem (if no further action is taken place) with the new maximum

contaminant level of 30 ppb in the Stage 2 of the USEPA's D/DBP rule (Arora et al., 1997). In addition, haloacetic acids could be naturally formed in the atmosphere during the photochemical degradation of chlorinated solvents (Frank et al., 1994). Because of their wide spread occurrence, toxicity to plants and aquatic organisms, and most importantly their suspected human carcinogenicity, there is a great deal of need to find treatment methods for haloacetic acids.

Ozonation is one of the most economical treatments since the operation is quite simple and no other chemicals accept ozone is needed. Ozonation system has currently been used in several water treatment plants (Li et al., 2004). The attractive property of ozone is its potent oxidizing power. It has a standard reduction potential, under an acidic condition, of about 2.1 volts, almost two times higher than that of O_2 (1.2 volts). It is also readily dissolved in water. Therefore, it can react fashionably fast with soluble organic compounds and oxidize them to smaller or less toxic molecules (Gottschalk, 2000). Recent studies have shown that ozonation is effective in removing a wide variety of chlorinated organic contaminants (Adams et al., 1997; Dilmeghani and Zahir, 2001; Jung, 2001). Owing to these backgrounds, ozonation shows a promise as a possible treatment for haloacetic acids.

Biodegradation of haloacetic acids is also an alternative for haloacetic acids reduction. A small number of studies reported that haloacetic acids could be naturally removed by aerobic biodegradation processes (Boethling and Alexander, 1979; Ellis et al., 2001). Several aerobic bacteria degrade haloacetic acids and use them as either cometabolites (Weightman et al., 1992) or as a sole carbon and energy source (Olaniran, 2001). In water treatment system, biodegradation is typically found associated with the application of granular activated carbon (GAC) that has already been used to remove NOM, precursors of haloacetic acids and other DBPs. After a long running period, GAC usually has natural bacteria population on its surface, and eventually works as biological activated carbons (BAC). GAC with a biomass that shows high biological activity is then called BAC (USEPA, 2001). Currently, there is very few number of information on the efficiency of BAC in removing haloacetic acids, despite the high potential of the method. The primary objective of the study was to investigate the efficiency in the removal of HAA_5 by the integrated treatment system combining ozonation and BAC column. Effects of ozone dose and contact time during the ozonation process and the impact of the empty bed contact time of the BAC column were also evaluated.

3.2 Materials and methods

3.2.1 Sample preparation

The synthetic samples of HAA_5 (CAA, DCAA, TCAA, MBAA, and DBAA) were used as feed solutions in this experiment. Samples were prepared using a commercially available HAA_6 standard (Supelco). Three initial HAA_5 concentrations, 60, 90, and 120 ppb were tested.

3.2.2 Ozone-BAC system

A Schematic diagram of the ozone-BAC testing unit used in this experiment is shown in Figure 3.1.
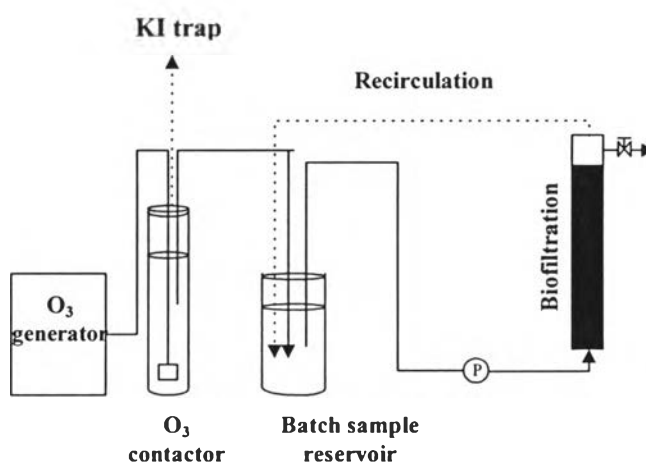

Figure 3.1: A Schematic diagram of ozone-BAC testing unit

The Ozone-BAC treatment system components were made of stainless steel, glass, and Teflon. The system includes two basic components: ozone contactor and biological activated carbon column. Both components were simultaneously used to conduct batch experiments studying the HAA_5 removal. HAA_5 sample solutions were first oxidized by ozone and then passed through the BAC column for further degradation.

3.2.2.1 Ozone contactor

All materials that contact with the water during the ozonation process are made of glass, PTFE, and stainless steel. The water sample was placed in a 5-L glass bottle and flowed to a 5-L ozone contactor by gravity. Ozone was generated from an ozone generator (Sky zone; star 04) that has the ozone generating capacity of 750 mg/hr. Ozone was introduced to the contactor by fritted glass disc at room temperature. The ozone dosage was varied in each experiment by changing the time of ozone production, while all settings on the ozonation apparatus remain the constant all runs. The residual ozone dosage was measured using the indigo trisulfonate method (Standard Methods, 1998). Off-gas from the ozone contactor was introduced to a potassium iodine solution (KI trap).

3.2.2.2 Biological activated carbon column

The granular activated carbon (GAC) media was packed into a glass column (50 cm high and ϕ 3 cm). An acclimated biofilm was established on the GAC media (Calgon F200) by seeding with raw water from Sam Sen raw water distributing canal (Klong Prapa) over a period of 1 year. The column was operated in an upflow mode by a peristaltic pump. Prior to the tests, the establishment of microbial communities in the BAC column was confirmed using the membrane filter technique. A steady colony count indicates the stability of the bacteria.

3.2.3 Operational conditions

A series of batch experiments were designed to measure HAA_5 removal as a function of ozone dosage, contact time of the ozonation process, and empty bed contact time (EBCT) of the BAC column. Three ozone doses, 0.5, 1.0, and 2.0 mg ozone/mg TOC were experimented with contact times varied from 5, 10, and 20 min. The effect of EBCT on BAC performance was investigated at 10, 20, and 30 min. HAA_5 concentration was measured from samples collected at the beginning of each experiment, after ozone contactor and after the BAC column. Additional samples (500

mL each) were also taken after the ozonation process and the BAC column for assimilable organic carbon (AOC) bioassay.

3.2.4 Analytical method

3.2.4.1 Determination of HAA$_5$

The amounts of HAA$_5$ were determined using USEPA method 552.2. Briefly, A 20 μl of 2, 3-dibromopropionic acid (10 μl/ml) was added in to a 40 mL of sample as a surrogate for QA/QC. Then the sample was adjusted to pH<0.5 by a concentrated H$_2$SO$_4$. Two grams of CuSO$_4$ was subsequently added to the acidic solution followed by Na$_2$SO$_4$ 16 g. The solution was then extracted with 4 mL methyl-tert-butyl ether (MTBE). Haloacetic acids that had been partitioned into the organic phase were converted to their methyl esters by the addition of 10% H$_2$SO$_4$ in methanol and warmed to 50 °C in water bath. The acidic extract was later neutralized by back extraction with a saturated solution of sodium bicarbonate. The target analytes were identified and measured by gas chromatography using electron capture detection (GC/ECD) Agilent GC6890. A DB-XLB (J&W Scientific) fused silica capillary column (30 m x 0.32 mm $i.d.$ x 0.05 μm film thickness) was used for the separation. The GC oven was temperature-programmed at 40 °C for 0.5 min and then from 40-200 °C at a rate of 15 °C/min, after that the temperature was held constant for 2 min. The injector was kept at 250°C, splitless mode, 30 sec purge activation time, and 50 pg per component. The detector temperature was maintained at 350°C, respectively.

3.2.4.2 Assimilable organic carbon (AOC) bioassay.

The AOC bioassay is an indirect or surrogate method to determine the potential for bacterial regrowth using *Pseudomonas fluorescens* Strain P-17 and *Spirillum.* Strain NOX (Standard methods, 1992)

Prior to the test, residual chlorine in a 500-m sample was neutralized by 0.5 mL sodiumthiosulfate solution (30 g/L). The sample was then pasteurized in a 70 °C water bath for 30 min. After being cool, the sample was inoculated with the 500 colony-forming units (CFU/mL) of the surrogate bacteria, and incubated at 15 °C for 1

week. Enumeration of bacteria was done by the spread plate method for 3 dilutions. Plates were incubated at 25 °C for 3 to 5 day before colony counting. Mean and the number of colonies of each strain were converted to the corresponding AOC values by the following equation (Standard methods, 1992);

$$\mu g \ AOC/L = [(mean \ P\text{-}17 \ CFU/mL)(2.44 \times 10^{-7}\mu g \ acetate\text{-}C/CFU)$$
$$+ (mean \ NOX \ CFU/mL)(3.45 \times 10^{-7}\mu g \ oxalate\text{-}C/CFU)]$$
$$(1000 \ mL/L)$$

3.3 Results and Discussion

3.3.1 HAA$_5$ removal by ozonation

Ozonation experiments were carried out with three concentrations of HAA$_5$, 60, 90, and 120 ppb. Results of the experiments shown in Figure 3.2 indicatded that ozonation is ineffective in removing HAA$_5$ under the test condition (pH ~6). As demonstrated in the figure, removal efficiencies in all ozonation experiments range between 10-20%. Comparable results were previously observed by Fu et al., (2002). The 10% reduction of CAA after 1-hr ozonation at pH 3.1 was reported. As illustrated in the Figure 3.2, an increase in ozone dose and contact time did not substantially improve the decomposition of HAA$_5$ by ozone. The decomposition of HAA$_5$ by ozonation process follows the first-order behavior which is described as;

$$\ln \frac{[HAA_{5t}]}{[HAA_{50}]} = -kt$$

as demonstrates in plots between $1/\ln(HAA_{5t}/HAA_{50})$ and contact time in Figure 3.3 . The apparent rate constant of the reaction which is defined as varies from 0.001 min^{-1} to 0.003 min^{-1} (plots between $[HAA_{50}\text{-}HAA_{5t}]$ and $1/[HAA_{50}\text{-}HAA_{5t}]$ are not linear indicating that the reaction is neither zero nor second order (Figure A1 and A2 in appendix A).The slow reaction between dissolved ozone and HAA$_5$ could due to chemical properties HAA$_5$ and the condition of the experiment. Reactions of ozone can occur via direct and indirect mechanisms (Langlais et al., 1991). The direct mechanism includes the reaction of dissolved ozone itself with a target compound.
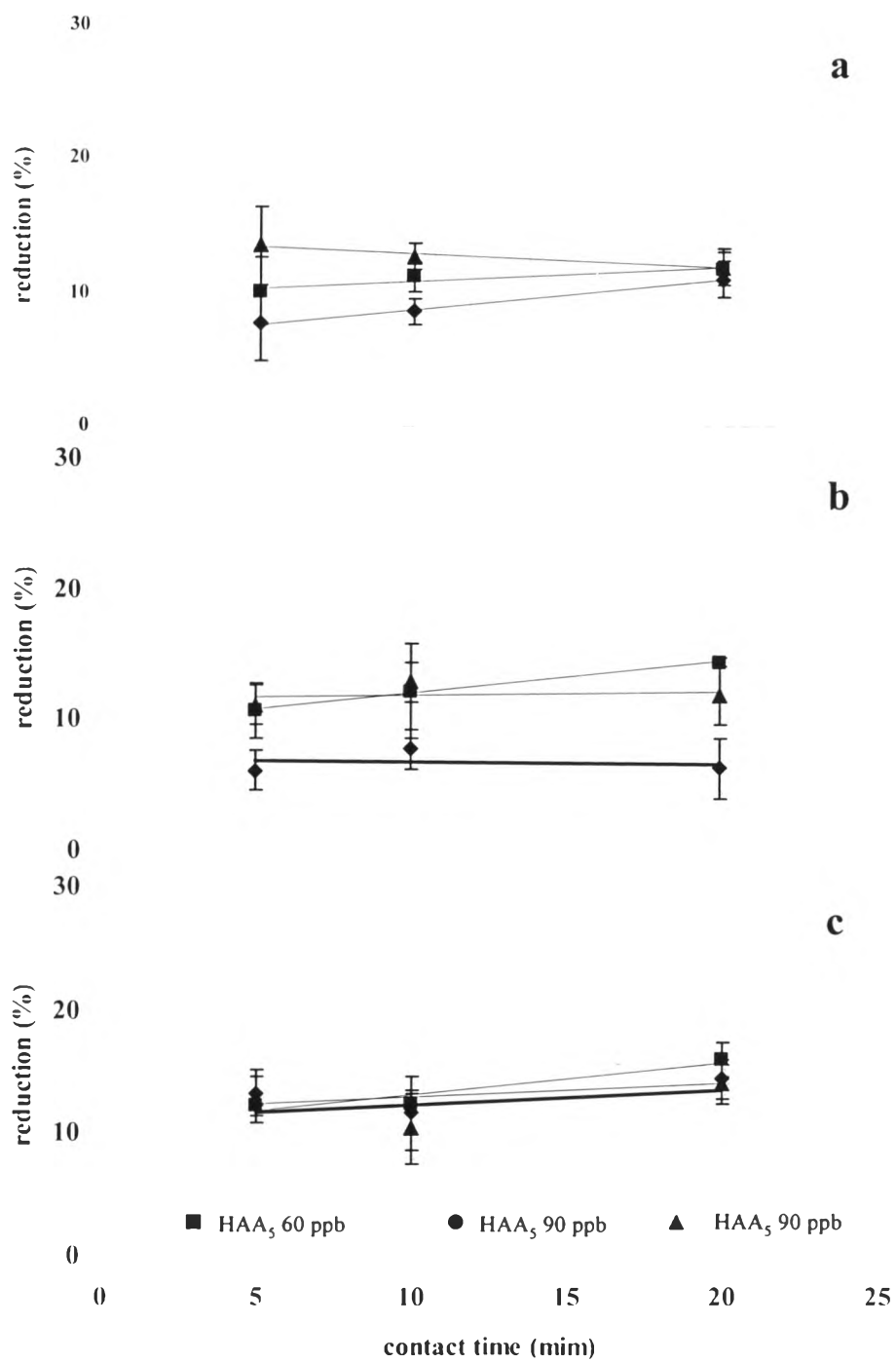
Figure 3.2: Efficiency of ozonation process in removing HAA_5, a) ozone dose 0.5 mgO_3/mg C, b) ozone dose 1 mgO_3/mg C, c) ozone dose 2 mgO_3/mg C
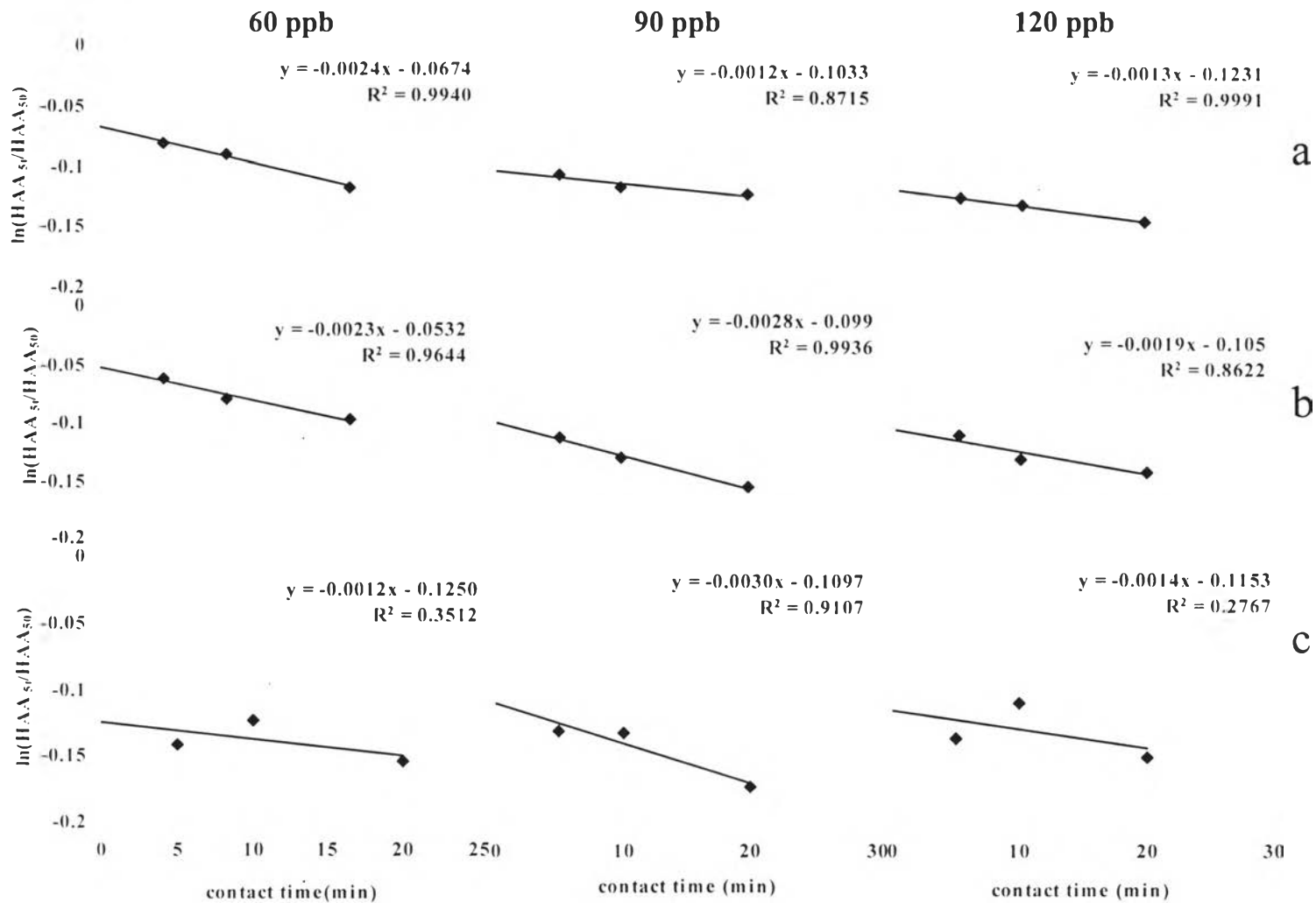
Figure 3.3: The first-order conversion of HAA$_5$ during ozonation; a) ozone dose 0.5 mgO$_3$/mgC, b) ozone dose 1 mgO$_3$/mgC, c) ozone dose 2mgO$_3$/mgC.

The indirect mechanism relies on the disintegration of dissolved ozone into hydroxyl radicals (OH$^\bullet$). These radicals are very short-living species but because of their higher reduction potential (2.9 volts), they are far more reactive than ozone itself (reduction potential 2.1 volts; www.lentech.com, 2005). Practically, both reaction mechanisms occur concurrently in a solution. However, one type of reactions will dominate, depending on conditions of the reaction. Basic condition promotes the dissociation of ozone to OH radicals; hence the indirect mechanism is predominant at high pH (Wang et al., 2005). In this study, pH of the feed HAA$_5$ solutions was around 6. Under this condition, it is more likely that the majority of dissolved ozone reacted with HAA$_5$ via the direct mechanism.

The direct mechanism of dissolved ozone can further be classified into three processes due to the ability of ozone to act either as 1,3-dipole, electrophilic, or nucleophilic agent during reactions (Langlais et al., 1991). The characteristic of ozone as a dipole molecule leads to a cyclo addition (criegee mechanisn) between ozone and saturated compounds (containing double or triple bonds) (Langlais et al., 1991). The high reduction potential of ozone makes it an excellent electrophile readily attacking compound with high electron density via an electrophilic reaction. In addition, ozone can also act as a nucleophile. The reaction of dissolved ozone based on this property mainly takes place at an electron deficit site of the target compound, particularly at a carbon center adjacent to an electron withdrawing group. The nucleophilic reaction is the most likely mechanism described the reaction between HAA$_5$ and ozone since HAA$_5$ contain COO$^-$, chlorine, and bromide; all are electron withdrawing groups. The reaction proceeded very slowly because nucleophilic reaction of ozone is less preferable than other mechanisms (Jung, 2001). The rate of nucleophilic reaction between ozone and electron withdrawing groups is exceptionally slow (Adam et al., 1997). Slow reaction rates observed in this study might be typical of the reaction between dissolved ozone and haloacetic acids and perhaps other alkyl carboxylic acids. The attempt to remove CAA and oxalic acid were succeeded only when catalyst was used during the ozonation process (Fu et al., 2002; Pine and Reckhow, 2002). Ozone uptakes are plotted in Figure 3.4.

Ozonation of HAA$_5$ occurred selectively. From Figure 3.5, it can be seen that among the degraded 10-20 % of HAA$_5$, CAA and BAA are the two primary HAA$_5$ species that were removed during the ozonation process. Other HAA$_5$ species remain

relatively unchanged, particularly TCAA. The low reactivity of ozone toward TCAA, DCAA, and DBAA indicates that number of electron withdrawing substituent (i.e. chlorine and bromide) have an effect on the removal of HAA_5 by ozonation. Steric effect is known to lower the rate of nucleophilic reaction (Larson and Weber, 1997). Urbansky (2001) noted that two halogen atoms are sufficient to offer stability to the center carbon. Therefore, both di- and trihaloacetic acids do not readily undergo a nucleophilic reaction (Urbansky, 2001), especially in acidic condition similar to this experiment. From these results it has been demonstrated that ozonation alone is not a good candidate for a treatment technique to remove HAA_5 at a pH range that is typically found in a water treatment system.
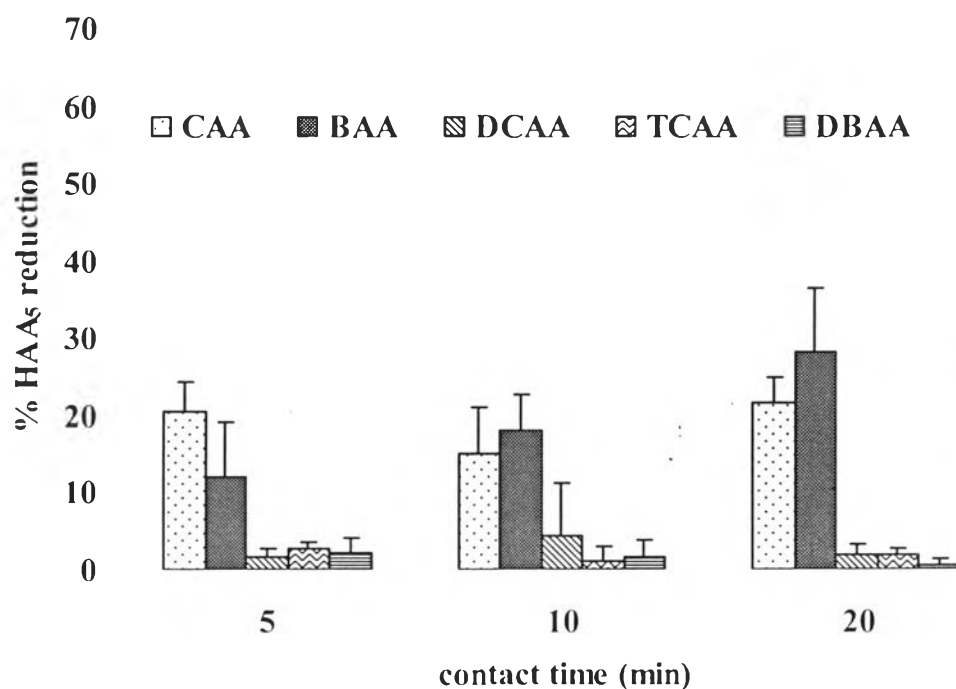

Figure 3.4: Removal of HAA species by ozonation.

3.3.2 HAA₅ removal by Biological activated carbon (BAC)

Ozonation is apparently ineffective for HAA₅ removal, only 10-20% of HAA₅ were removed. In order to further improve the treatment efficiency, a BAC column was installed to subsequently treat the effluent from the ozone contactor. Prior to entering the BAC column, residual ozone in the solution was removed by letting the sample sit for 45 min. Residential time of the ozonated water samples in the BAC column was varied by adjusting the empty bed contact time (EBCT). The efficiency of the BAC column in removing HAA₅ is shown in Figure 3.6. Contrasting to the ozonation process, BAC is very effective in removing HAA₅. A complete removal of the acids was observed in nearly all experimental conditions. Plots in Figure 3.6 also demonstrated that EBCT of the samples is the important factor regulating HAA₅ reduction. The longer the solution stays in the column, the better the HAA₅ removal will be. In this study, an EBCT of at least 20 min is required to remove 90-100% HAA₅ in the test solutions.

The removal of HAA₅ via the activated carbon adsorption is considered less likely. Before starting the experiment the BAC column had been continuously fed with raw water for water supply production for one year. It is more likely that the majority or perhaps all surface area of the activated carbon had already been occupied by bacteria. The direct adsorption of HAA₅ on activated carbon, therefore, would be limited as the carbon's surface area was already exhausted. Results from several studies (Summer, 1989; Hsin-hsin 2004; McRae et al., 2004) support this assumption as it has been found that the adsorption capacity of virgin GAC (nonacclimatized BAC) was much lower than BAC. The assumption is also substantiated by the fact that GAC is typically considered ineffective in removing haloacetic acids in water treatment system. This is because haloacetic acids are hydrophilic and exist in ionized forms at the pH range of portable water (Xie and Zhou, 2002). More importantly, recent study showed that the degradation of BAA by the autoclaved BAC was negligible whereas the original BAC exhibited 100% removal efficiency (Xie and Zhou, 2002).
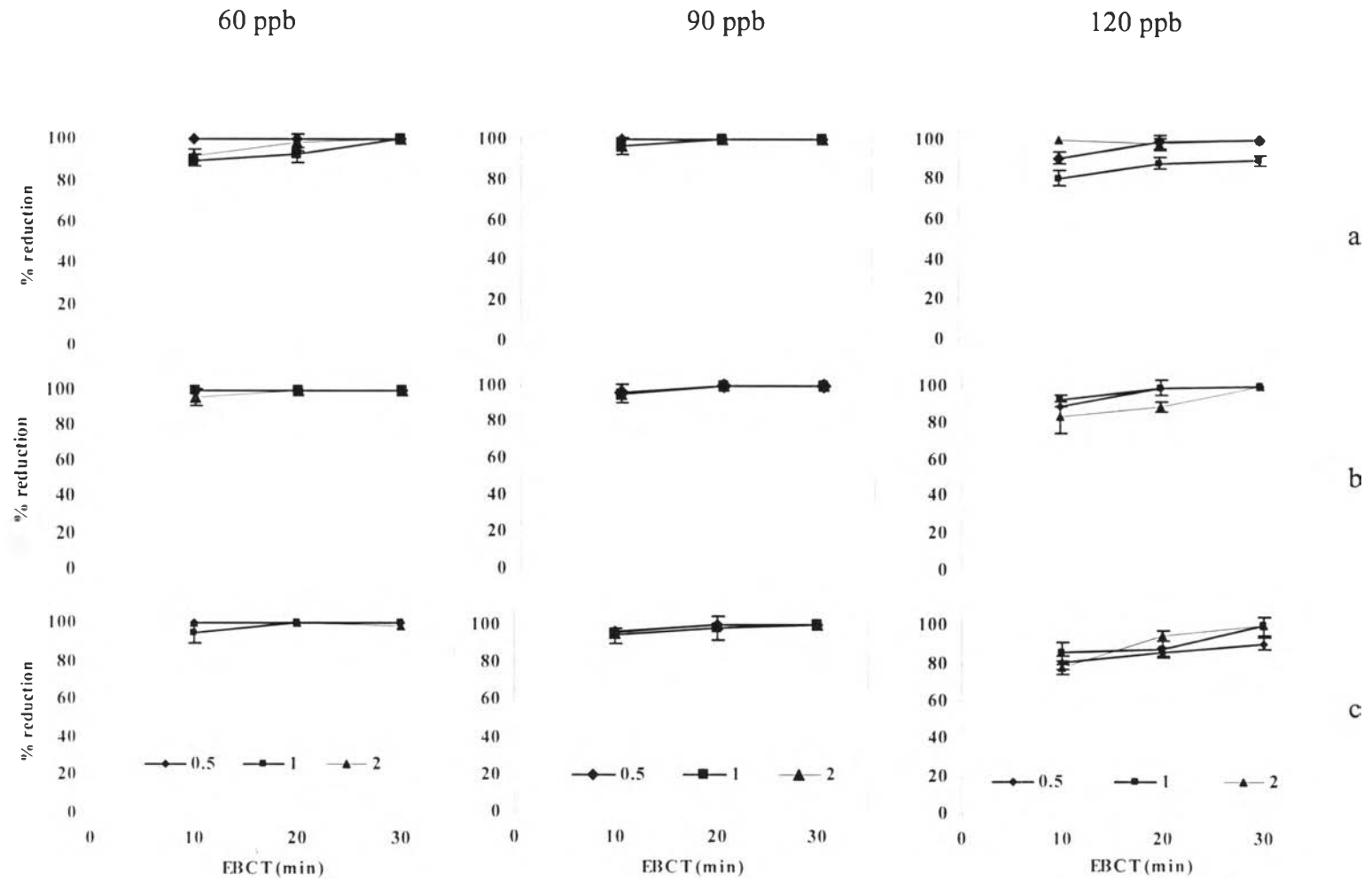
Figure 3.5: Efficiency of BAC column in removing HAA_5 after pretreated with ozone dose 0.5, 1, 2 mgO_3/mgC, a) ozone contact time 5 min, b) ozone contact time 10 min, c) ozone contact time 20 min.

The microbial decomposition of haloacetic acids such as CAA, BAA and TCAA at the concentration found in natural water and in the drinking water distribution systems has been reported by McRae et al. (2004). In a batch experiment, CAA was rapidly degraded by the CAA enrich culture at concentrations ranging from 5.7 ppb to 148 ppb. The ^{14}C radiolabeled CAA experiment further revealed that 79% of ^{14}C was converted to CO_2 and the remaining was incorporated into biomass. Similar results were observed with BAA and TCAA. Interestingly, it was observed that the biodegradation rate of CAA is comparable to that of BAA. This suggests that the biodegradation pathways of CAA and BAA might be similar. However, McRae et al., (2004) also reported that TCAA culture can also completely degraded CAA and BAA, but no TCAA degradation by CAA culture was observed. Since microorganism used in McRae et al. (2004) were separated from raw water, it is unambiguous that microorganisms capable to biodegrade multiple haloacetic acids are available in water environment.

Rapid biodegradation of HAA_5 by the BAC column rather suggests that the BAC column alone could be able to remove HAA_5 in the initial feed solution. As high as 54-108 ppb of HAA_5 remained in the feed solution after ozonation process (values calculated from 10% HAA_5 removal efficiency of the ozonation process) and was subsequently biodegraded by bacteria in the BAC column.

3.3.3 Assimilable organic carbon (AOC)

The primary reason to add ozonation in the experiment is to assists the BAC process by reducing molecular size and altering functionalities of HAA_5. Both functions are typically occurred during the ozonation process (Gilbert, 1979). Oxidation by ozone normally increases the amount of biodegradable organic carbon or assimilable organic carbon (AOC). AOC refers to the fraction of the dissolved organic carbon that can be used by the bacteria for growth and cell maintenance. Many recalcitrant natural organic matters (NOM) are more readily biodegradable after treated by the ozonation process (Huck, 1999). Oxidation by-products, such as aldehydes, keto acids, and carboxylic acids are formed when ozone reacts with NOM. If microbial degradation is promoted, these compounds will serve as substrate for

microorganisms that will further convert them to carbon dioxide and water (Koffskey and Lykins, 1999).

The AOC bioassay is an indirect or surrogate method based on colony-forming units (CFU) of the bioassay organisms. The assessment of AOC concentration is based on growth measurements of two selected pure cultures: *Pseudomonas fluorescens* strain P17, and a *Spirillium* sp. strain NOX (Standard method, 1992). In this study, the AOC values of the sample after ozonation and BAC column were measured and compared. Figure 3.7 presents the AOC values before and after the BAC column. Samples collected before entering the BAC column were the ozonated solutions sitting for 45 min to allow the dispersion of dissolved ozone. It can be seen from the figure that most AOC values of sample solution after passing through the BAC column are higher. This outcome is not expected since the amount of AOC should decrease after biofiltration. This irregularity was hypothesized to be due to the formation of intermediate species during HAA biodegradation. *Pseudomonas* sp. strain DCA1 degrades chloroacetic acid and produces glycolic acid as an intermediate. This intermediate is also found in the degradation pathways of other haloacetic acid degraders, such as *Xanthobacter autitropicus* GJ10 and *Ancylobacter aquaticus* AD 25 (Hage and Hartmans, 1999). The degradation pathway of indigenous bacteria in natural surface water should involve the formation of similar intermediates. The microcosm study using pond water to investigate fate of CAA, DCAA and TCAA reported that biodegradation of all three haloacetic acids led primarily to the formation of chloride and oxalic, glyoxalic, and glycolic acids that are degraded more readily than their parent compounds as shown in Figure 3.7. Hence, if such intermediates were formed during the degradation of HAA$_5$ by bacteria in the BAC column, the AOC surrogate bacteria should favor these intermediates more than HAA$_5$ in sample solutions before passing the BAC column (samples after ozonation). Nevertheless, in this study AOC might not be a useful indicator for the ozone-BAC system that is used for controlling HAA$_5$ because oxidation of HAA$_5$ by ozone is relatively ineffective.
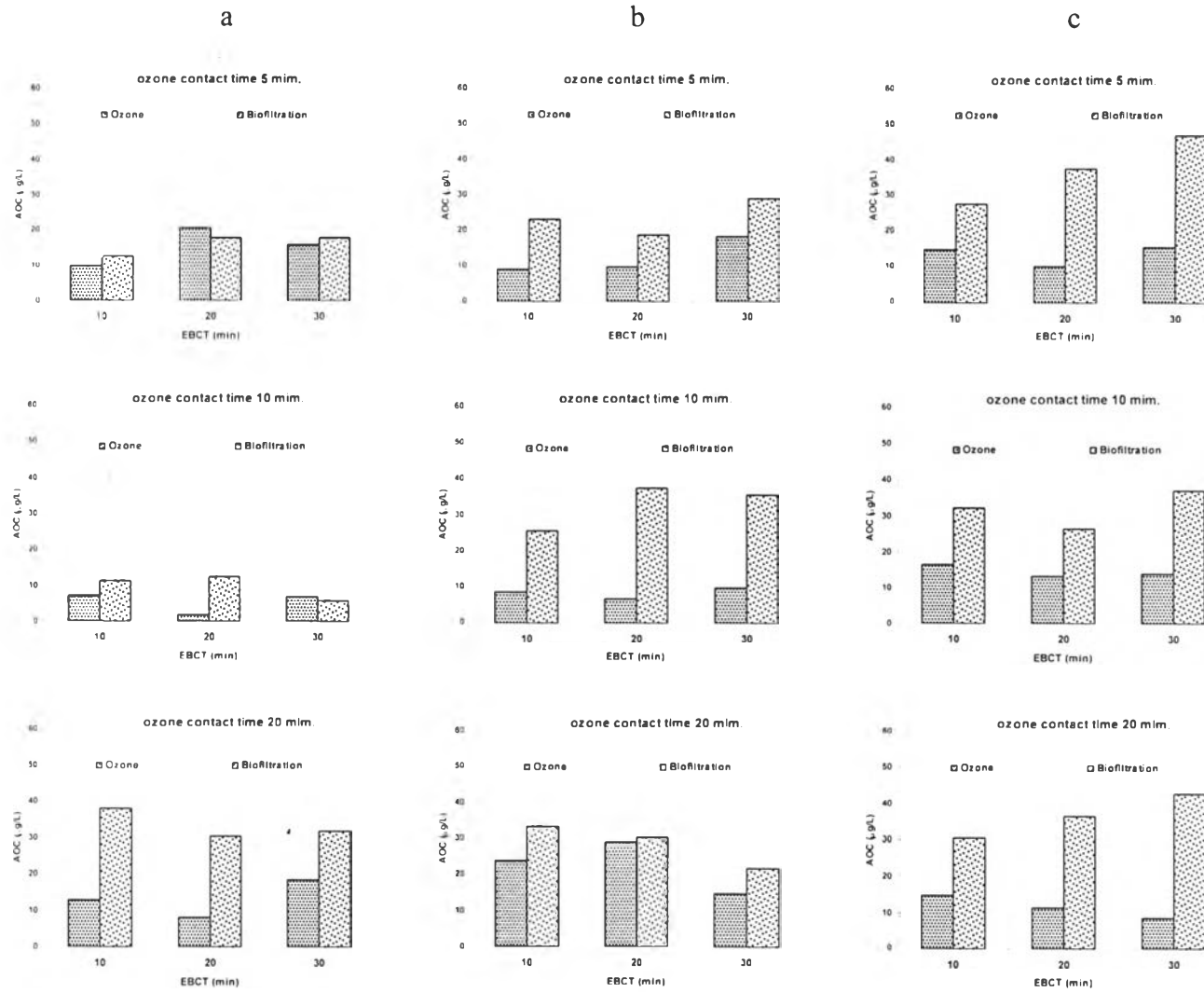
Figure 3.6: AOC measured after ozonation and BAC column; a) ozone dose 0.5 mg O_3/mgC, b) ozone dose 1.0 mg O_3/mgC, c) ozone dose 2.0 mg O_3/mgC
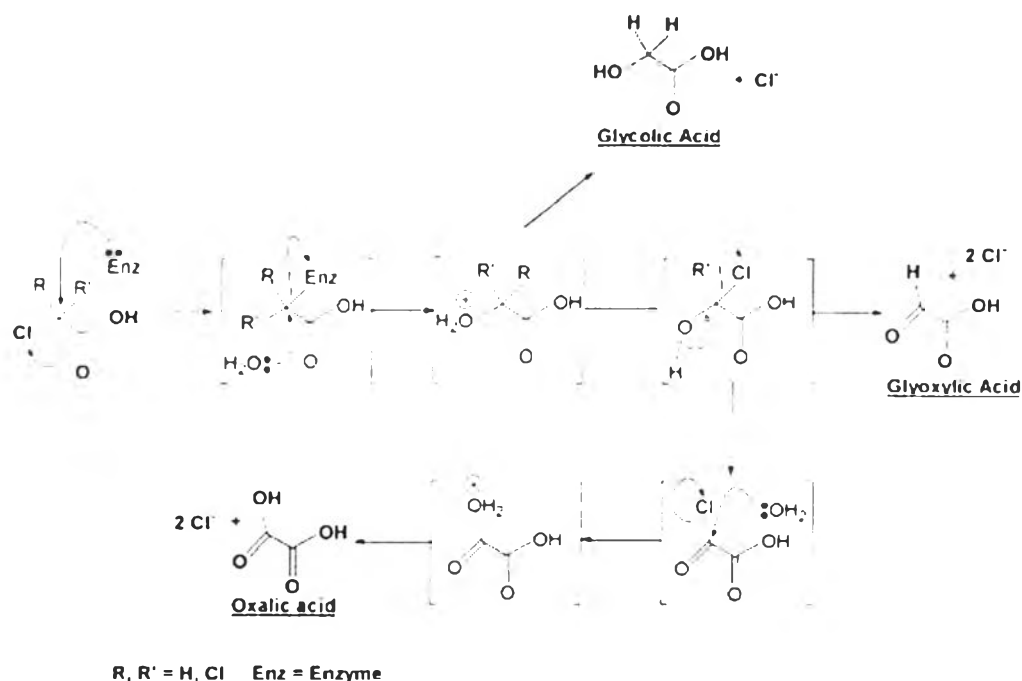
Figure 3.7: The degradation pathway of CAA, DCAA, and TCAA (Ellis et al., 2001)

3.4 Conclusions

It has been demonstrated that the removal of HAA5 by the ozonation process is not an effective approach. Less than 20 % of HAA5 at the concentration level found in surface and drinking water system was removed by the process. HAA5 with multiple halogen atoms are more persistent to dissolved ozone than monohalogenated species. Since HAA5 with multiple halogen atoms such as DCAA and TCAA are group B, probable human carcinogens, the ozonation process actually has little effect in minimizing the toxicity of HAA5. In contrast, the BAC column inoculated with bacteria readily available in surface water exhibited a superior performance. It can remove 90-100% of HAA5 with an EBCT of 20 min or more. With its rapid HAA5 removal, it was anticipated that the BAC column alone should probably be able to eliminate HAA5 up to 100 ppb without the assistance from the ozonation process. Indigenous microorganism communities in surface water inoculated on the BAC column can degrade individual HAA5 species with no preference. Based on satisfactory results from the BAC column, it is more likely that the natural HAA biodegradation should already occur in the surface water environment. However, whether this capability exists in microbial communities in the water supply distribution system needs to be identified.